18. Kinetics of Stress Build-up in Glasses by Ultra-violet Irradiation

Stress in Glass Caused by Ultra-violet Irradiation (Part 8)

By

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Stress build-up in glasses by ultra-violet irradiation was observed and related phenomena were investigated by the authors[1]. It was confirmed that the stress build-up is caused by contraction (density increase) of glasses by ultra-violet ray. For practical purposes it is important to find methods for preventing stress build-up or fracture of glasses. On the other hand, from theoretical point of view, it is also an interesting problem to clarify the mechanisms of stress build-up or structural change of glasses by ultra-violet ray.

Investigation of reaction kinetics or of factors which affect reaction rates is often an efficient mean to determine the mechanisms of chemical reaction. In this note, results of experiments on time-(dose rate)-stress relations in some borosilicate glasses irradiated by ultra-violet ray are reported.

Compositions of glasses used for the experiments are represented in Table 1. Three of the glasses were commercially available and the other one was prepared in laboratory scale. Polished columns (10×15×5 mm) of the glasses were irradiated by 400 W mercury discharge lamp made of silica glass. Length of the lamp was 150 mm and outer diameter of the lamp was 17 mm. During irradiation, the columns were cooled by air flowing around them. Stress at irradiated surfaces was measured by photoelastic method at certain intervals.

Table. 1. Composition of Glasses (wt%)

Glass No.	SiO_2	B_2O_3	Na_2O	K_2O	Li_2O	Al_2O_3	BaO	$Fe_2O_3+As_2O_3$
1	80.5	12.0	4.0	0.5		2.5		0.3
2	80.5	12.0	4.0	0.2		2.5		<0.1
3	65.5	18.0	2.0	3.0	1.0	7.5	3.0	$(+Sb_2O_3)$0.3
4	73.5	20.0	6.5					0.02

1 : Terex, 2 : Pyrex, 3 : Kovar sealing glass

Time-stress relations in the glasses are shown in Fig. 1. In the figures, l's denote distances between axis of the lamp and the irradiated surfaces of the columns. When the column was not cooled, the stress was partly released by slight rise of temperature and was kept at rather low value (dashed curves in Fig. 1). After irradiation of about 800 hrs, Stresses S seemed to reach at value of saturation S_∞. Relations between l and S_∞ in the glasses are shown in Fig. 2.

From the experimental results (Fig. 1 and 2) it is seen that: 1) There are induction periods of about 100 hrs at the start of every irradiation test, 2) In the next stage, the rate of stress build-up increases and is approximately inversely proportional to l, 3) After irradiation of about 800 hrs, S almost reaches to constant value S_∞, and 4) S_∞ is approximately inversely proportional to l.

Assume approximately that the diameter and the length of the light source are infinitely small and long, respectively. The problem of propagation of light flux from the source is uniform in the direction parallel with the axis of the lamp and is reduced to a two-dimensional problem in a cross section perpendicular to the axis. Light flux which passes outward per unit time through unit area of the irradiated surfaces of the glass columns is inversely proportional to l. Dose rate I is, therefore, inversely proportional to l, too. It thus seems that S_∞ and initial rate of building-up of stress are both proportional to I (or I^1).

Induction periods, saturation of reaction and I^1-dependence of reaction rate and S_∞ are commonly observed in photochemical and photo-sensitized catalytic reactions[2]. Possible interpretations of the

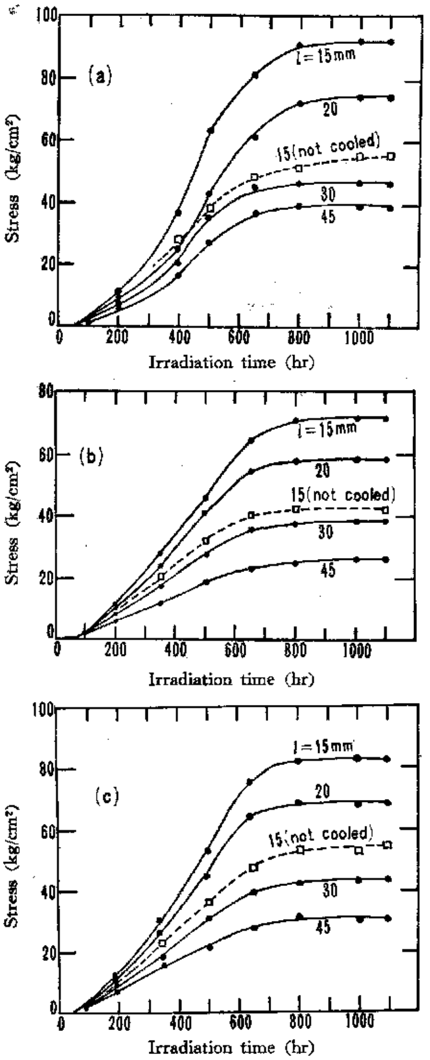

Fig. 1. Irradiation time-stress relations in a) Terex, b) Pyrex and c) Kover sealing glasses l: distance between axis of the lamp and irradiated surfaces

experimental results are, for example, as follows:

1) Induction period is the time in which slight tension is built up and thus new freedom for subsequent structural change of glass is produced: or it is the time in which number of sites in glass which can prevent or compensate the effect of irradiation is reduced to zero, and

2) After irradiation for long time, severe tension is formed and futher increase of the tension is prevented by backward reaction. Saturation of stress value is thus observed.

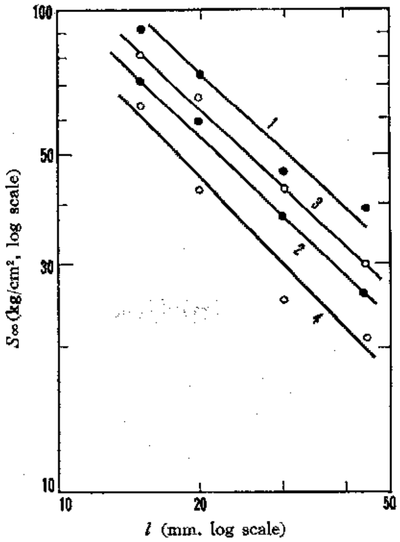

Fig. 2. Relation bewtween l and S_∞

Kinetics of stress build-up seem to be described by the following equations; namely,

$$dn/dt=\alpha I-\beta n-\gamma pn,\ dp/dt=-\gamma pn \cdots\cdots (1)$$

Here, α, β and γ are constants, respectively, t is time, n is number of sites which have changed their configuration by the action of ultra-violet ray, p is number of site which can compensate the stress build-up, and the stress S is assumed to be a linear function of n and p. αI, βn and γpn represent the rates of foreward, backward and compensation reactions, respectively, and $S=S_\infty$ corresponds to $n=\alpha/\beta$ and $p=0$.

If the rate constant of backward reaction is a function of I, following equations seem to be equally provable;

$$\left.\begin{array}{l} dn/dt=\alpha' I^2-\beta' In-\gamma pn',\ dp/dt=-\gamma pn' \\ \text{and when } n=\alpha'/\beta',\ S=S_\infty \text{ and } p=0 \end{array}\right\} \cdots (2)$$

The rates of foreward reaction αI and $\alpha' I^2$ are expected to correspond to one- and two-photon processes, respectively. For definite conclusions, detailed studies are necessary.

References

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2) For Example, G.M. Burnett, "Mechanism of Polymer Reactions" (1954); J.G. Calvert, J.N. Pitts, "Photochemistry" (1966).

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